



Short communication

Influence of the active mass particle suspension in electrolyte upon corrosion of negative electrode of a lead-acid battery



Yu. Kamenev*, G. Shtompel, E. Ostapenko, V. Leonov

The Scientific Technical Center ELECTROTYAGA Closed Jointed Stock Company, 50 A, Kalinin Str, St.-Petersburg 198095, Russia

HIGHLIGHTS

- We studied the influence of the particles of positive active mass suspension.
- Considerable increase of the Pb-electrode corrosion at the contact of slime particles.
- The appearance mechanism macro-defects on lugs of the negative plates is offered.

ARTICLE INFO

Article history:

Received 5 November 2013

Received in revised form

15 January 2014

Accepted 23 January 2014

Available online 4 February 2014

Keywords:

Lead-acid battery

Corrosion tests

Positive active material

Negative lug corrosion

ABSTRACT

The influence of the suspension of positive active mass particles in the electrolyte on the performance of the negative electrode in a lead-acid battery is studied. A significant increase in the rate of corrosion of the lead electrode is shown when slime particles get in contact with its surface, which may result in the rise of macro-defects on the lugs of the negative electrodes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

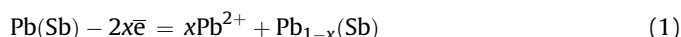
There has been a great of research on the corrosion of positive electrodes in lead-acid batteries [1–3], but the common perception is that negative electrodes would not corrode because such electrodes involve a reduction reaction. There are reports showing that negative electrodes corrode under special circumstances [4–8].

This is accounted for by the fact that the corrosive decay of the negative grid lugs is one of the most frequent causes of failures of lead-acid batteries. The corrosive process taking place on the negative grids under cathodic protection arises when electrolyte fills thin gaps where straps are cast onto the grid lugs. Omae et al. [4] hypothesized that local corrosion processes develop in such gaps due to a shift of potential in the positive direction along the gap. The rate of this corrosion may be up to 0.4–0.5 mm/year at 20 °C, and it grows as the temperature rises [4]. The corrosion

products have a greater specific volume than that of the initial lead, and it creates mechanical breaking force which affects lugs and strap interface.

It is possible to prevent corrosive and mechanical decay of the lugs/strap joint by selecting correct casting-on temperatures and compositions of alloys that lugs and strap are made of, thereby providing a positive meniscus without gaps in the cast-on joints [6].

One more cause of corrosion of negative grids made of Pb–Sb alloy is the contact corrosion, which is another type of local corrosion. The structure of Pb–Sb alloy consists of a solid solution of antimony in lead, eutectic, and phase inclusions of antimony which appear because of dissociation of the oversaturated solid solution during its cooling. Therefore, the alloy surface is rather uniformly covered with short-circuited galvanic cells. Under these circumstances, lead basically undergoes oxidation:



while on antimony the process of reduction of hydrogen takes place:

* Corresponding author. Tel.: +7 812 786 77 67 (work); fax: +7 812 786 97 05 (work), +7 812 295 16 63 (home).

E-mail address: batteryprof@bk.ru (Y. Kamenev).



Since the overpotential of hydrogen evolution on antimony is rather moderate, the rate of reaction (2) rate will be substantial. On the Pb/Sb contact point a steady potential is formed, being positive with respect to the equilibrium potential of lead and being negative with respect to the equilibrium potential of antimony. As the distance from the contact point increases, the potential will be shifting to the negative into the depth of lead, and at a certain distance it will reach the equilibrium potential of this metal. As to antimony, the further inside it, the more the potential will be shifting to the positive, converging to the equilibrium potential of this metal. The distance at which the changes of potentials take place depends on the electrical conductivity of the electrolyte. In a discharged battery when the electrical conductivity of acid is low, the area of contact corrosion is small, whereas in a charged battery it spreads to noticeable distance. In order to preclude the development of contact corrosion, alloys with a low content of Sb or Pb–Ca are being used in modern lead-acid batteries.

When a lead-acid battery is being used, its charged positive active mass (PAM) consisting mainly of PbO_2 , may partially shed fine particles of lead dioxide (FPLD) which may further be carried to the negative grid by the flow of the electrolyte. This process should be most noticeable in batteries with agitated electrolyte. ‘Bubbling’ and ‘Airlift’ agitation systems used nowadays have been described in paper [9]. Agitating creates electrolyte flows capable of carrying FPLD from the positive electrode to the lugs of the negative electrode. FPLD can have either temporary short-term contact with the lugs of the negative electrode, or they can get fixed thereon in rough places, pits or cracks. In any case, the contact of PbO_2 particles with the lugs of the negative grid creates appropriate conditions for the development of contact corrosion of the negative electrode lugs.

The effect of FPLD on the rate of corrosion of the negative electrode lugs is studied in this paper.

2. Experimental

The electrode made as a rectangular strap of pure lead was placed into a sulphuric acid solution (4.87 mol l^{-1}). The surface of the electrode had been previously cleaned and polished. The

electrode potential was measured in three conditions: 1) in non-agitated electrolyte; 2) in agitated electrolyte; 3) in agitated electrolyte with FPLD suspension.

FPLD was added into the electrolyte on the basis of 40 g l^{-1} . The slime assay showed that it contained 91–92% PbO_2 and 6–7% PbSO_4 . The temperature in the cell was maintained at 20°C . The duration of measurement of potential was 24 h.

The corrosion tests of lead electrodes were carried out in the following modes.

Mode 1 (reference mode). Corrosion test of a lead electrode in $4.87 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$. Duration of testing was 340 h; at a normal room temperature. The weight of the electrode was 32.058 g, the total surface was 7.52 cm^2 .

Mode 2 (simulation of functioning of the negative grid with FPLD fixed on its surface). The surface of the lead electrode was covered with FPLD. To ensure reliable fixing, the electrode was wrapped with a layer of AGM separator on top. The resulting construction was placed horizontally into a solution of $4.87 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$. Corrosion tests continued for 340 h. The weight of the electrode was 33.623 g; the total surface was 8.74 cm^2 .

Mode 3 (simulation of functioning of the negative grid in the flow of electrolyte with FPLD suspension). Corrosion testing of the lead electrode was carried out in agitated electrolyte with FPLD suspension. FPLD content in electrolyte was 40 g l^{-1} . Agitation continued for 48 h. The weight of the electrode was 73.051 g; the total surface was 17.05 cm^2 .

After testing, all the samples were washed in alkaline solution with an addition of sugar to remove the corrosive film, and the loss of electrode weight was determined. FPLD were analysed for the content of PbO_2 and PbSO_4 .

3. Results and discussion

Fig. 1 shows the variation of potential of the lead electrode in sulphuric acid solution in the non-agitated and in the agitated electrolytes, and also in the agitated electrolyte with FPLD suspension. It can be seen from the figure that the potential of the lead electrode in the non-agitated electrolyte steadily retains the value at about -0.305 V (hereinafter the potential values are given in regard to the normal hydrogen electrode). After being kept in the non-agitated acid for 24 h, the potential of the lead electrode was 0.304 V .

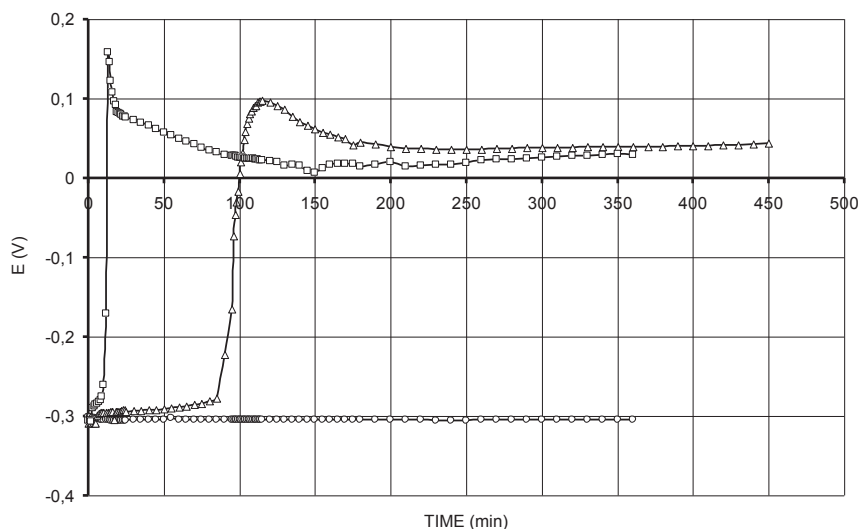
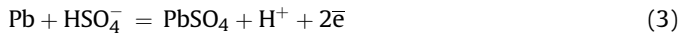


Fig. 1. The potential of the lead electrode during its retention in electrolyte. Testing modes: 1) electrode kept in non-agitated electrolyte ($\circ$), 2) electrode kept in agitated electrolyte ($\triangle$), 3) electrode kept in agitated electrolyte with FPLD suspension (40 g l^{-1}) ($\square$).

In the agitated electrolyte the potential grew slowly from -0.308 V to -0.286 V during 1.5 h. After that, the potential behaved as follows: 1) a sharp rise of potential to the value of 0.10 V; 2) the potential passes its highest level; 3) the potential comes to an almost constant level at 0.05 V. After being kept in the agitated electrolyte for 24 h the potential of the lead electrode showed 0.095 V.

After adding FPLD powder into the agitated electrolyte, the potential grew from -0.305 V to 0.160 V over approximately 10 min. Then the potential gradually decreased and came to an almost constant level of 0.035 V. After being kept in the agitated electrolyte with FPLD suspension for 24 h, the potential of the lead electrode showed approximately 0.090 V.

The equilibrium potential of the lead electrode in sulphuric acid solution



is equal to -0.304 V. Beside that, the following reactions can take place on the lead electrode:



which result in its depolarization and spontaneous sulphating. The rate of reactions (4) and (5), according to [10], can be calculated using the following equations:

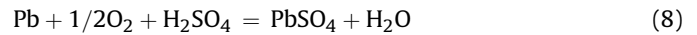
$$i_{\text{H}} = a_{\text{H}_2\text{SO}_4}^{0.25} \cdot \exp\left[\frac{5815 \cdot (0.356 - a)}{T}\right] \quad (6)$$

$$i_{\text{O}} = \frac{1.93 \cdot 10^5 \cdot C_{\text{O}_2} \cdot D_{\text{O}_2}}{\delta} \quad (7)$$

where $a_{\text{H}_2\text{SO}_4}$ – is the activity of sulphuric acid in the solution, a – is the constant in the Tafel equation for the process of cathodic hydrogen evolution on lead, C_{O_2} – is the concentration of dissolved oxygen, D_{O_2} – is the diffusion coefficient of dissolved oxygen, δ – is the thickness of the diffusion layer.

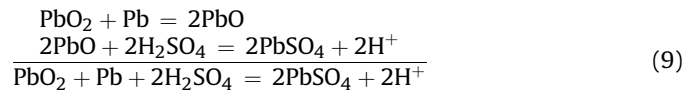
In the non-agitated electrolyte the values of i_{H} and i_{O} are extremely low due to a high overpotential of hydrogen evolution on lead ($a = 1.5$ V), a low solubility of oxygen ($C_{\text{O}_2} = 6.5 \cdot 10^{-7}$ mol cm $^{-3}$) and a low diffusion coefficient ($D_{\text{O}_2} \approx 10^{-5}$ cm 2 s $^{-1}$). All this results in a low depolarization of the lead electrode in the non-agitated electrolyte, and in its potential steadily staying on the level of equilibrium (3). This situation can be seen in Fig. 1.

In the agitated electrolyte the value C_{O_2} increases due to accelerated transfer of the surface layer of the electrolyte rich with oxygen to the surface of the electrode, and the value of δ decreases. All this results in an increase in the oxygen reduction rate and in a higher polarization of the lead electrode. Together with the growth of i_{O} , the lead sulphation process with oxygen depolarization takes place according to the following scheme:



According to [11], alkalization of the solution takes place in the film pores, which promotes formation of basic lead sulphates in them. Thus the lead electrode transforms from a close to equilibrium state (3) into a state of salt passivity which is characterized by a sharp shift of the potential to the value of 0.05 – 0.09 V. The stability of the passive state of the lead electrode is determined by the balance between oxygen reduction current and chemical dissolution of the sulphate film.

When FPLD particles are added to the solution, a rapid shift of potential to the positive direction up to approximately 0.16 V takes place, which indicates a strong depolarizing effect of the lead dioxide particles. In the agitated electrolyte it took about 110 min to come to a passive state, whereas in the agitated electrolyte with slime particles it took only about 5–10 min. The polarization effect of FPLD is determined by the fact that when FPLD particles get in contact with the surface of the lead electrode, a short-circuited cell evolves and the following process takes place



The process behaviour in equation (9) is confirmed by the results of chemical analysis of the composition of the initial FPLD

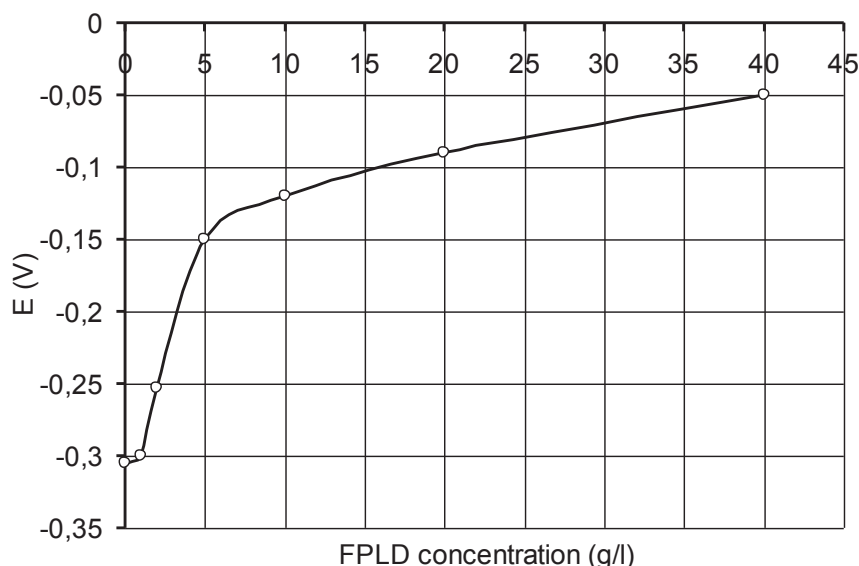


Fig. 2. Dependence of the potential of the lead electrode on the slime concentration, at its highest point after adding FPLD into the electrolyte.

particles and the particles composition after the described test was completed. The initial FPLD assay was 92% PbO_2 and 7.4% PbSO_4 , whereas after the test it showed 84% PbO_2 and 15.4% PbSO_4 . The decreased content of lead dioxide in FPLD and the increased content of lead sulphate is the result of FPLD particles reduction when they get in contact with the lead electrode.

The decrease of potential in the agitated solution with FPLD suspension after its passing the peak, as shown in Fig. 1, is associated with the reduction of the surface of lead dioxide particles and with the formation of a non-conductive lead sulphate layer on it. It reduces the concentration of reactive FPLD and reduces the depolarization effect.

Fig. 2 shows the behaviour of the potential of the lead electrode in the agitated electrolyte at its peak, which follows the moment when FPLD was added into the solution, depending on its quantity. It can be seen from the figure that an increase of FPLD concentration in the solution results in a growth of the potential of the electrode.

Fig. 3 shows a potentiodynamic curve taken on the lead electrode within the range of $-0.70 \div 0.40$ V at the rate of 10^{-3} V s^{-1} in the solution of $4.87 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. Comparing Figs. 2 and 3, it is possible to estimate, to a first approximation, the behaviour of the lead electrode depending on the content of reactive FPLD in the electrolyte. For example, when the content of FPLD in the electrolyte is $1\text{--}3 \text{ g l}^{-1}$, the potential of the electrode is approximately $-0.3 \div -0.2$ V, which corresponds with the range of active lead. When the concentration of FPLD is over 15 g l^{-1} , the lead electrode potential is higher than -0.10 V, which in the case of this experiment corresponds to the passive state of the lead electrode.

The depolarizing effect of FPLD should have its influence upon the rate of corrosion of the lead electrode. As mentioned above, in the non-agitated electrolyte the rate of lead corrosion is extremely low because of the high overpotential of hydrogen evolution on lead and a low solubility of oxygen in the electrolyte.

The agitation of electrolyte, and especially with lead dioxide particles in it, depolarizes the electrode which should incite the rate of corrosion of the lead electrode.

In accordance with the procedure described above, corrosion testing of lead electrodes was carried out in the solution of 4.87 mol l^{-1} sulphuric acid, in non-agitated electrolyte and in agitated electrolyte with FPLD suspension (40 g l^{-1}). In the course

Table 1

Results of corrosion tests.

Test mode	Rate of corrosion	
	$\text{g/g}_{\text{sample}} \cdot \text{h}$	$\text{g}(\text{cm}^2_{\text{sample}} \cdot \text{h})^{-1}$
Lead electrode in non-agitated acid.	$3.81 \cdot 10^{-6}$ (100%)	$1.60 \cdot 10^{-5}$ (100%)
Lead electrode in agitated acid with FPLD suspension	$9.98 \cdot 10^{-6}$ (263%)	$4.23 \cdot 10^{-5}$ (265%)
Lead electrode covered by FPLD, in acid	$9.32 \cdot 10^{-6}$ (245%)	$3.61 \cdot 10^{-5}$ (225%)

of testing, FPLD in the cell was periodically renewed. Furthermore, a corrosion test of a lead electrode covered with FPLD layer was carried out. The tests were made at a normal room temperature. The results of the tests are shown in Table 1. It can be seen from the Table that with FPLD suspension in the electrolyte the rate of corrosion of the lead electrode increased 2.6 times. It is also noticeable that the effect of FPLD is almost the same, regardless of whether it is suspension or coating.

Fig. 4 shows defects taking place on the lugs of negative electrodes of lead-acid batteries of high capacity where electrolyte agitation system is incorporated. It can be seen from the picture that the defect has a tendency to grow. Initially, it is a small pit on the side edge of the lug, and it considerably grows with time. It should be mentioned that these defects have been noted only on the outside edges of the negative electrodes' lugs facing the tank walls. These are exactly the areas most exposed to the flow of agitated electrolyte carrying FPLD particles, and it makes possible to take into account the described mechanism of growth of the rate of corrosion of the negative electrodes' lugs coming from their contact with FPLD.

When a real lead-acid battery is in operation, FPLD particles may deposit on local rough areas of the lugs and thereby accelerate the corrosion rate on the lugs alloy and extend the defect. Later on during charging, FPLD particles and the products of its interaction with lugs alloy (PbSO_4 , $\text{nPbO} \cdot \text{PbSO}_4$, PbO) should be reduced to spongy lead (Pb), thereby activating the surface of defects. During a later stand-by of the battery, still more FPLD would deposit on the defects, increasing their corrosion still further. In such a way, the defect may assume a considerable scope, negatively affecting the performance of the negative electrode and the lead-acid battery on the whole.

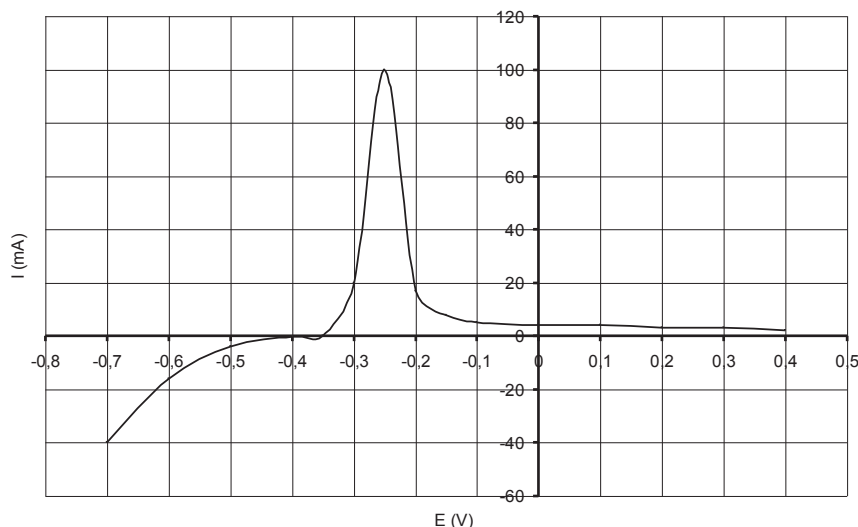


Fig. 3. Potentiodynamic curve for the lead electrode in sulphuric acid specific gravity 1.28 g cm^{-3} . Scanning speed 10^{-3} V s^{-1} .

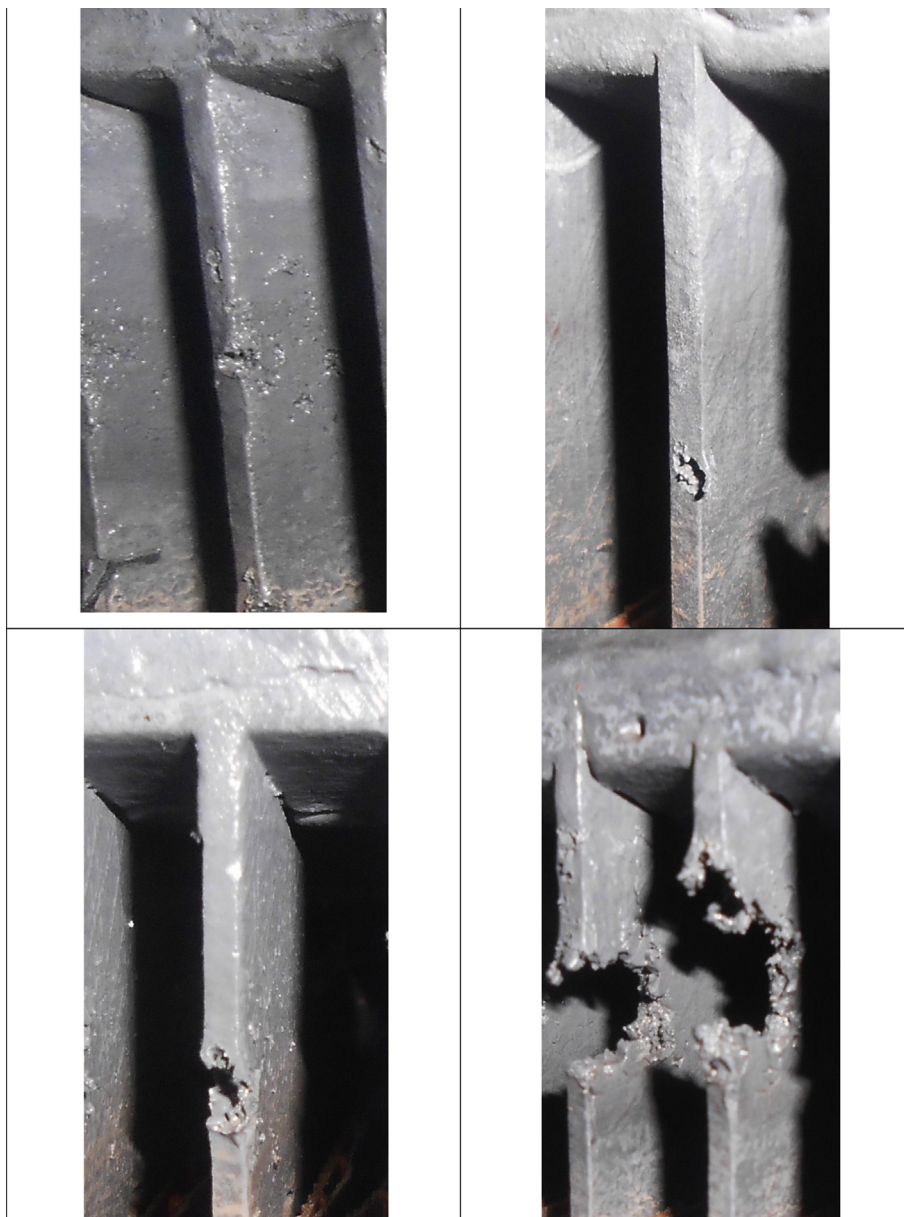


Fig. 4. Appearance of defects on the lugs of negative electrodes.

4. Conclusion

In this paper we have investigated the effect of the positive active mass particles that constitute a suspension in the electrolyte, on the functioning of the negative electrode in a lead-acid battery. We have showed that when such particles get in contact with a lead electrode, its corrosion rate increases considerably, which may result in arising macro-defects on the lugs of the negative electrodes.

References

- [1] P. Ruetschi, J. Power Sources 127 (2004) 33–44.
- [2] K. Sawai, Y. Tsuboi, S. Osumi, J. Power Sources 175 (2008) 604–612.
- [3] Y. Mi-Lin, Z. Wen-Zhen, J. Power Sources 195 (2010) 631–637.
- [4] T. Omae, S. Osumi, K. Takahashi, M. Tsubota, J. Power Sources 65 (1997) 65–70.
- [5] S. Hue, J. Power Sources 45 (1993) 131–137.
- [6] D. Berndt, Maintenance-Free Batteries, Research Studies Press Ltd., John Wiley & Sons Inc, N.Y, 1997, p. 496.
- [7] E. Ernst, Electrochemical Investigation of VRLA (dissertation), Doctor-Technologies (Chemistry), Port Elizabeth Technikon, January 2004.
- [8] N. Koura, K. Kasuya, K. Ui, Y. Takiguchi, Y. Idemoto, Electrochemistry 73 (2005) 135.
- [9] Yu. Kamenev, A. Kiselevich, V. Leonov, Elektrohem. Energy 8 (2008) 140–145.
- [10] I. Aguf, Sb. Rab. Khim. IstochNIKam Toka N14 (1980) 10–12.
- [11] D. Pavlov, R. Popova, Electrochim. Acta 15 (1970) 1483–1491.